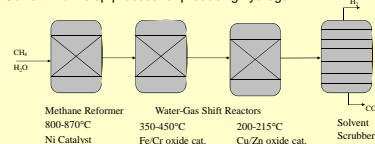


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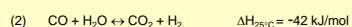
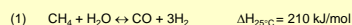
## Development of a Catalyst/Sorbent for Methane Reforming

### Introduction

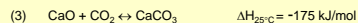
Current multi-step process for producing hydrogen:



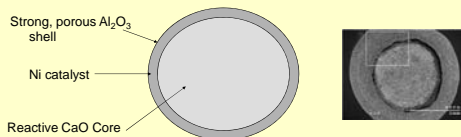
Process is based on the following reactions:



Proposed single-step process for producing hydrogen combines preceding reactions with the following reaction:



Single-step process is made possible by development of a combined catalyst and sorbent in the form of core-in-shell pellets.



Results of a laboratory scale demonstration with a reactor packed with these pellets are shown in Table 1 and are compared with and without  $\text{CO}_2$  absorption.

Table 1. Product gas composition (Dry Basis, mol %) resulting from reforming  $\text{CH}_4$  by using a 3:1 mol ratio of steam to carbon at 1.0 atm and 600°C

	With $\text{CO}_2$ Absorption	Without $\text{CO}_2$ Absorption
$\text{H}_2$	96.3	75.5
$\text{CO}$	1.3	7.2
$\text{CO}_2$	1.7	15.1
$\text{CH}_4$	0.9	2.3

### Overview

A combined catalyst and sorbent for reforming  $\text{CH}_4$  is being developed by encapsulating a  $\text{CaO}$  core in a porous alumina shell that supports a Ni catalyst all within a small spherical pellet.

### Sorbent Core Development

Need: A highly reactive material capable of withstanding repeated absorption of  $\text{CO}_2$  and regeneration over many cycles.

Results of cyclic absorption and regeneration tests conducted over 80 cycles at 750°C are shown in Figure 1 for 3  $\mu\text{m}$  limestone and -212/+63  $\mu\text{m}$  dolomite. The materials were precalcined at either 900°C for 3 hr or 1100°C for 5 hr. Results of similar tests conducted over 200 cycles with uncalcined and precalcined 3  $\mu\text{m}$  limestone are shown in Figure 2.

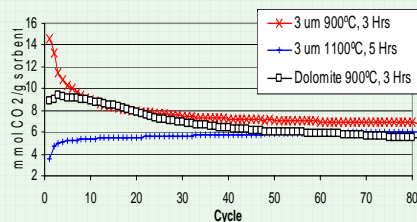


Figure 1. TGA results of cyclic absorption and regeneration tests made with precalcined limestone (3  $\mu\text{m}$ ) and dolomite.

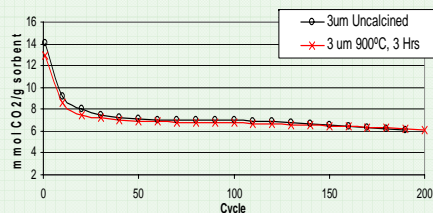


Figure 2. TGA results of cyclic absorption and regeneration tests made with both uncalcined and precalcined limestone (3  $\mu\text{m}$ ).

A comparison of the two sets of results suggests that the limestone has an ultimate absorption capacity of 6 mmol  $\text{CO}_2/\text{g}$  sorbent.

### Shell Development

Need: Strong, porous material with large surface area to support Ni catalyst.

Such material is made by calcining a mixture of crystalline and amorphous  $\text{Al}_2\text{O}_3$  powders with added  $\text{CaO}$  or  $\text{La}_2\text{O}_3$ . The effects of incorporating 5 wt% powdered limestone on cast 6 mm diameter cylindrical pellets of  $\text{Al}_2\text{O}_3$  are indicated by Figure 3. Results show maximum strength is obtained with 3  $\mu\text{m}$  size limestone.

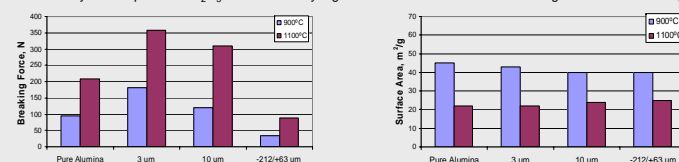


Figure 3. Breaking force and surface area of cast pellets with 5 wt% limestone of various sizes. Pellets were calcined at either 900°C for 3 hr or 1100°C for 2 hr before testing.

The effects of combining  $\text{Al}_2\text{O}_3$  with either  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{La}(\text{NO}_3)_3$  or  $\text{Ba}(\text{NO}_3)_2$  before preparing and calcining the cast pellets are indicated by Figure 4 for equivalent concentrations of additives. Results show  $\text{La}_2\text{O}_3$  provides a great increase in strength.

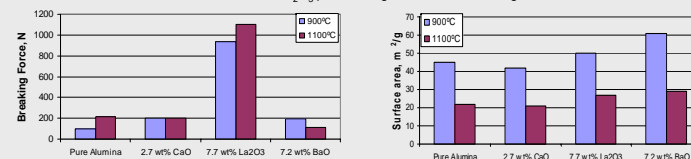


Figure 4. Breaking force and surface area of cast pellets made with equivalent concentrations of additives. Pellets were calcined at either 900°C for 3 hr or 1100°C for 2 hr before testing.

Core-in-Shell Pellets with different concentrations of  $\text{La}_2\text{O}_3$  in the shell produced the results indicated by Figure 5. Again 7.7 wt%  $\text{La}_2\text{O}_3$  produced a large increase in strength.

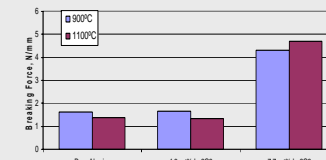


Figure 5. Breaking force of core-in-shell pellets with different concentrations of  $\text{La}_2\text{O}_3$  in the shell and calcined at different temperatures. Pellets were calcined at either 900°C for 3 hr or 1100°C for 2 hr before testing.

### Accomplishments, Present and Future

#### Sorbent Improvement

- Absorptivity of  $\text{CaO}$  declines with usage
- Rate of decline may be inhibited by  $\text{MgO}$
- Testing of sorbent with additive will be extended to 1000 cycles or more

#### Catalyst/Shell Improvement

- A promising shell material composed of  $\text{Al}_2\text{O}_3$  and  $\text{La}_2\text{O}_3$  has been formulated and subjected to limited testing
- The usefulness and durability of this material as a catalyst support and shell material will be thoroughly tested in the future

#### Performance Evaluation of Core-in-Shell Pellets

- Core-in-shell pellets combining the best formulations of the components will be prepared and evaluated by reforming  $\text{CH}_4$  at different temperatures and pressures
- Pellets will also be subjected to limited life-cycle testing

#### Application for the Water Gas Shift Reaction

- Pellets developed for reforming  $\text{CH}_4$  will also be tested for the reaction of  $\text{CO}$  and  $\text{H}_2\text{O}$